

2006 Annual DOE Fuel Cell Program Review

Effect of Fuel and Air Impurities on PEM Fuel Cell Performance

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FC#24

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Project Overview

Timeline

- Start: FY05
- Status: Ongoing

Budget:

FY06:
800K

Partners:

FreedomCAR and Fuel Partnership
USFCC

Barriers:

Electrode performance decreased by impurities (fuel cell efficiency decreases)

Higher Pt loading required to maintain performance in presence of impurities increases cost

Durability may decrease in the presence of impurities

Targets (2010):

- 5000 hrs durability
- 30\$/kW by 2010
- 55% energy conversion efficiency
- 0.3g/kW Pt loading

Project Objectives

Overall Objective: Contribute to the understanding of the effects of fuel and air impurities on fuel cell performance

Specific Goals:

Develop analytical methods for trace measurements

Test fuel cell performance under simulated multi-component hydrogen impurity gas mixtures

Investigate effect of impurities on catalysts and other FC components

Develop methods to mitigate negative effects of impurities

Develop models of fuel cell-impurity interactions

Continue collaborations with USFCC, Fuel Cell Tech Team, Industry and other National Laboratories to foster a better understanding of impurity effects

Impurities And Their Sources in Polymer Fuel Cells

- Fuel Impurities
- *Hydrogen Source and Reforming Process*

Natural gas
Coal
Fuel Oil \longrightarrow **CO, NH₃, H₂S, HC's**

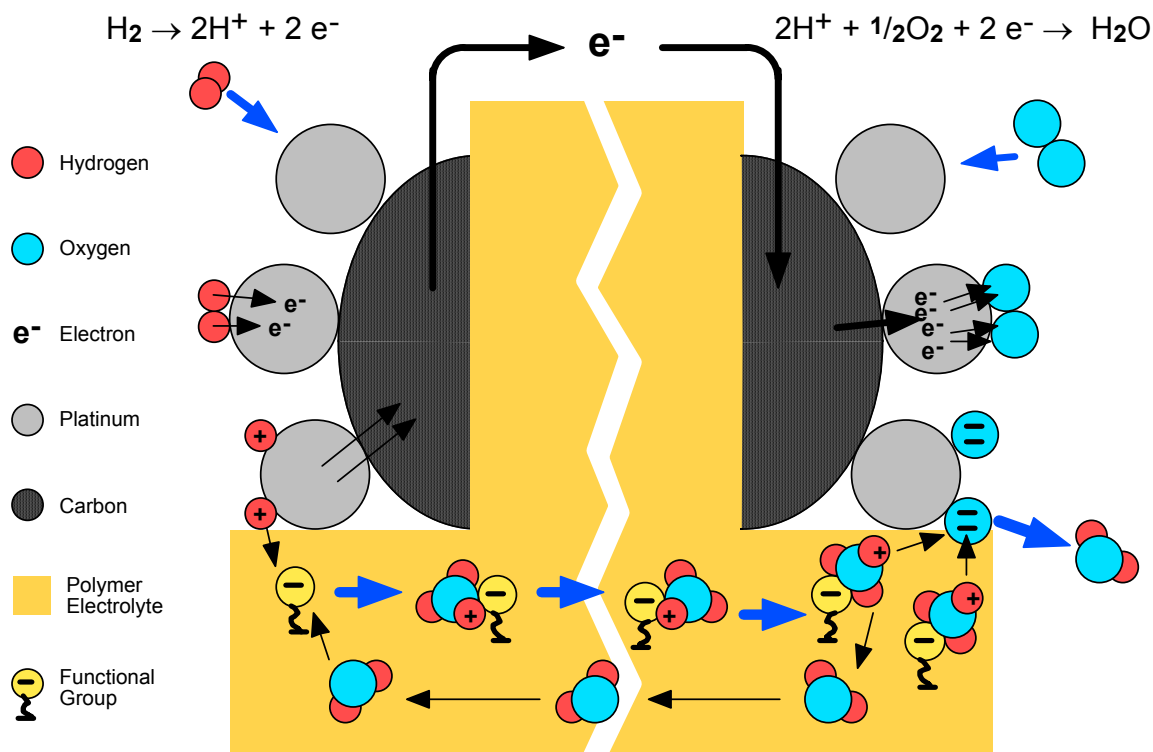
- Air Impurities
 - * *From fuel combustion pollution:* **SO₂, NO & NO₂, Soot**
 - * *From natural sources:* **Ocean salts, dust**

- Other
 - * *De-icers:* **NaCl, CaCl₂**
 - * *Corrosion products from FC system:* **cations**

Recent FC-Tech Team focus on gas mixtures to simulate common fuel impurities

Understanding Impurity Adsorption Effects

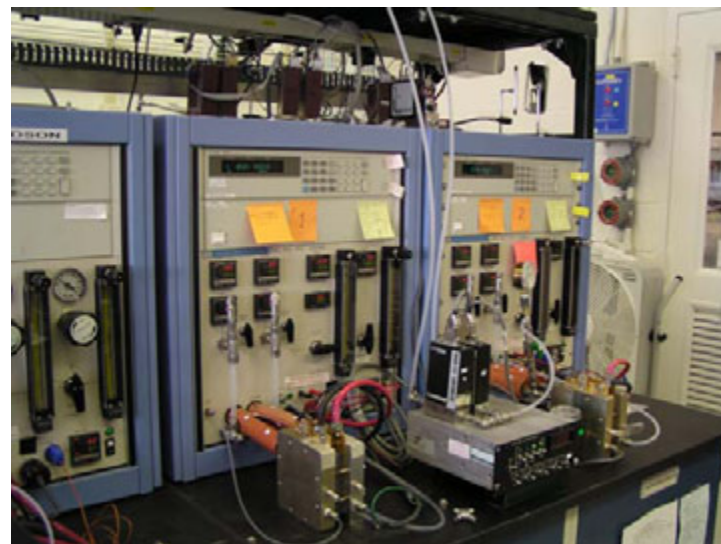
- Impurities may adsorb onto:
 - Pt surface
 - CO, H₂S, SO₂, Cl⁻
 - Carbon support
 - H₂S, SO₂
 - Ionomer
 - M⁺, NH₄⁺
 - Gas diffusion layer
 - Salts, wetting agents



- Impurities may block reaction sites for: **chemisorption, charge transfer** and/or **impede protonic conduction**.
- May also **change GDL properties** affecting mass transport

Research Approach

- Fabricate and operate fuel cells under controlled impurity gases
 - Multi-gas mixing manifolds and FC test stations
 - Pre-blend impurity gas
 - Measure performance
 - Understand degradation mechanisms
 - Study mitigation approaches
- Develop analytical tools for studies
 - Electroanalytical methods
 - *In situ* diagnostics
 - Sub PPM gas analysis
- Analyze and model data

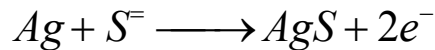


Analytical Method Development

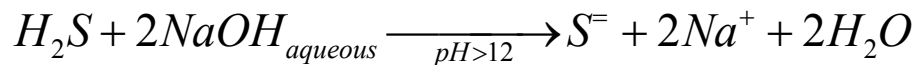
H₂S Detector and TPD

- We have developed a reliable low cost method for sub-ppm H₂S analysis- ppb sensitivity

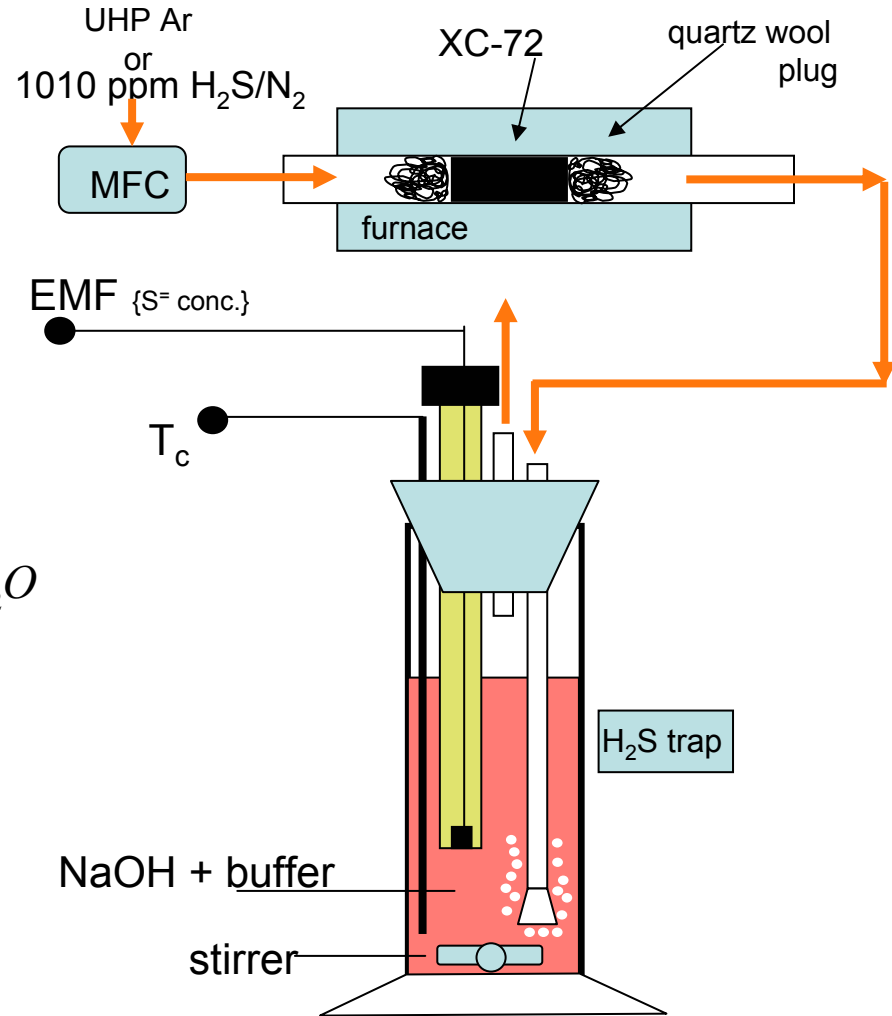
- Ag/AgS Electrode Sulfide ion probe
- Detects S⁼



- Probe measures ppb quantities of H₂S by S⁼ concentration change

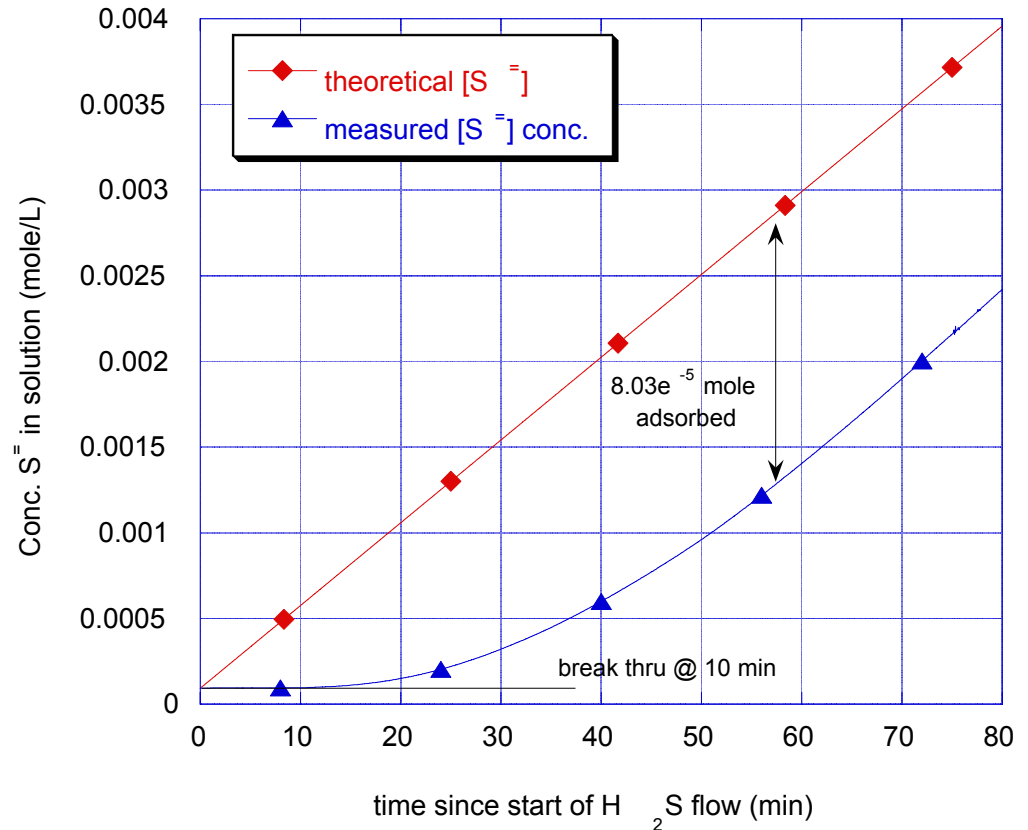


- H₂S is a sticky gas: care must be taken in ppb measurements
 - Pre-treat gas lines
- Temperature Programmed Desorption performed by heating sample at 5° C/min.

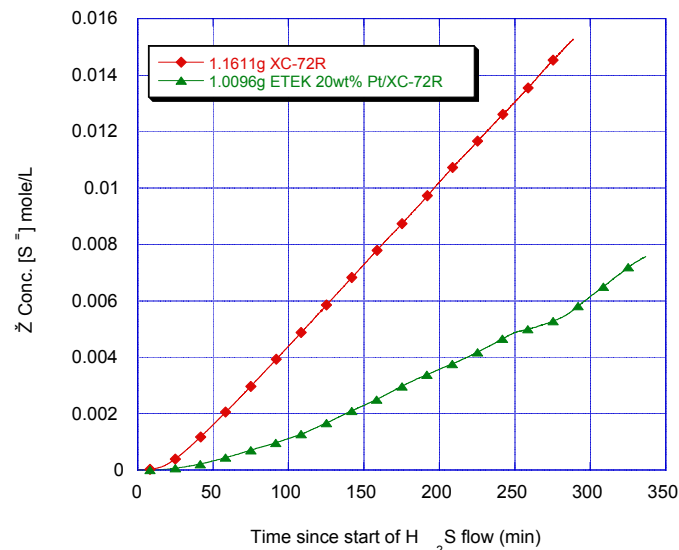
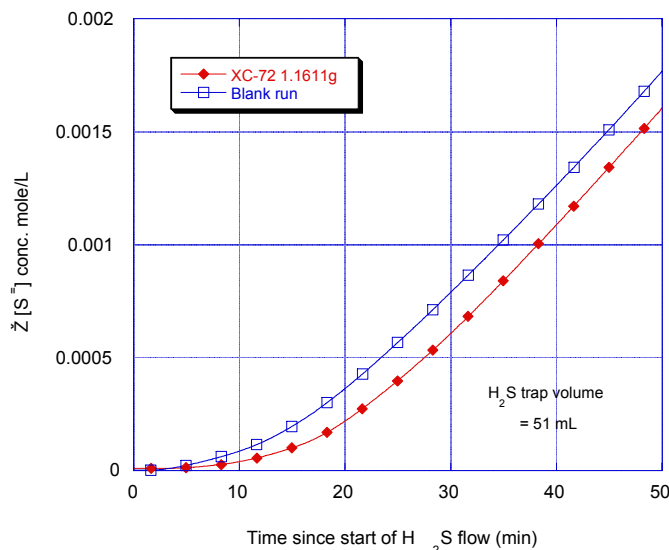


XC-72R Comparison To Activated Carbon

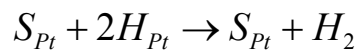
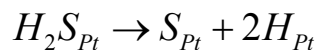
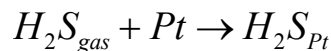
- First experiment repeated using activated charcoal
- 0.24 wt% or 80 times greater absorption than on XC-72R form of carbon
- *Form of carbon is very important in determining H_2S adsorption behavior*



H₂S Adsorption On XC-72 Carbon and E-TEK™ Pt/XC-72 Results



- XC-72 absorbs little H₂S at RT
- *Pt 20%XC-72 adsorbs significant amounts of H₂S*
 - ~2%
 - Process exhibits slow kinetics- H₂S dissociative adsorption?



- Desorption temperature >200° C

Hydrogen Impurity Mixture

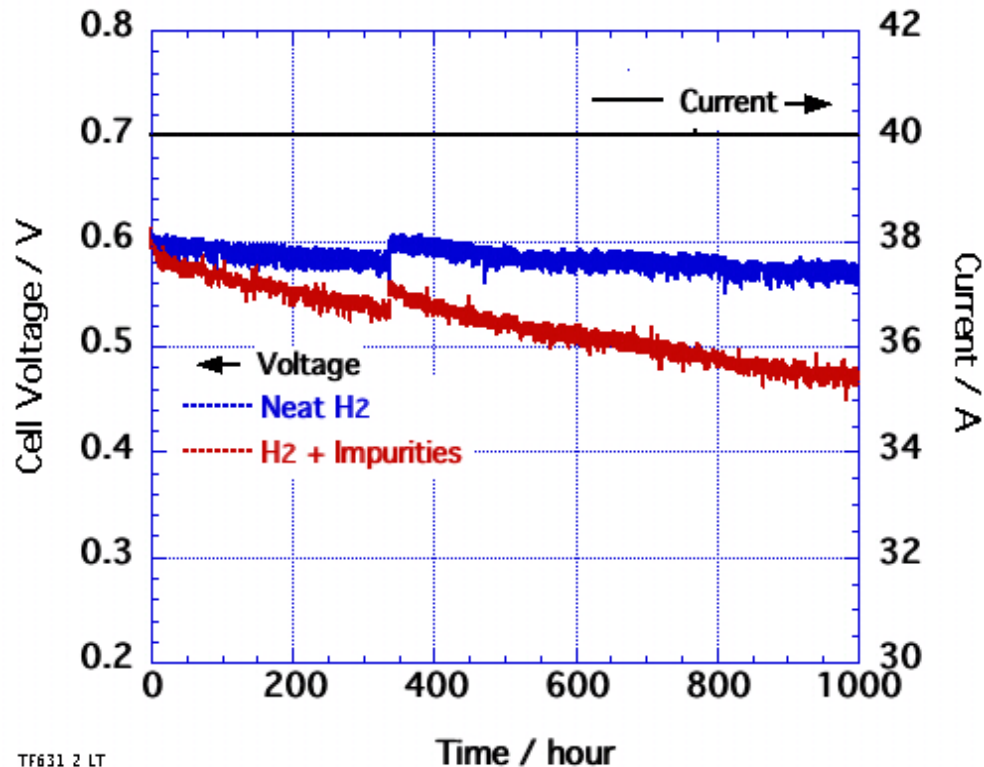
FreedomCar Fuel Cell Tech Team proposed hydrogen impurity spec.

<i>Component</i>	<i>Level</i>	<i>LANL Test</i>
Hydrogen	> 99.9	95-99 *
Sulfur (as H ₂ S)	10 ppb	10 ppb
CO	0.1 ppm	0.1 ppm
CO ₂	5 ppm	5 ppm
NH ₃	1 ppm	1 ppm
NMHC	100 ppm	50 ppm ethylene
Particulates	Conform to ISO 14687	not included in first test

*** Includes dilution due to inert gas in stock mixtures**

Milestone: Constant Current Testing of Impurity Mixture

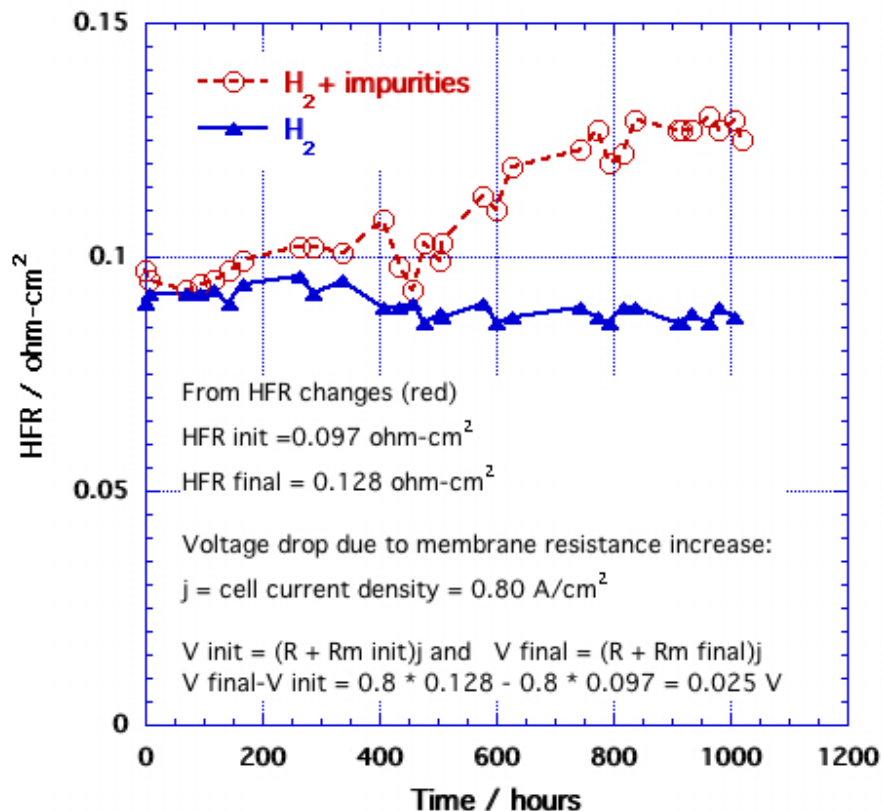
Voltage losses of two 50 cm² equivalent cells run at 0.8 A/cm² for 1000 hours



- Impurity cell performance loss is significantly greater than hydrogen control cell*

TF631 2 LT

Impurity Mixture Effects On Membrane Conductivity

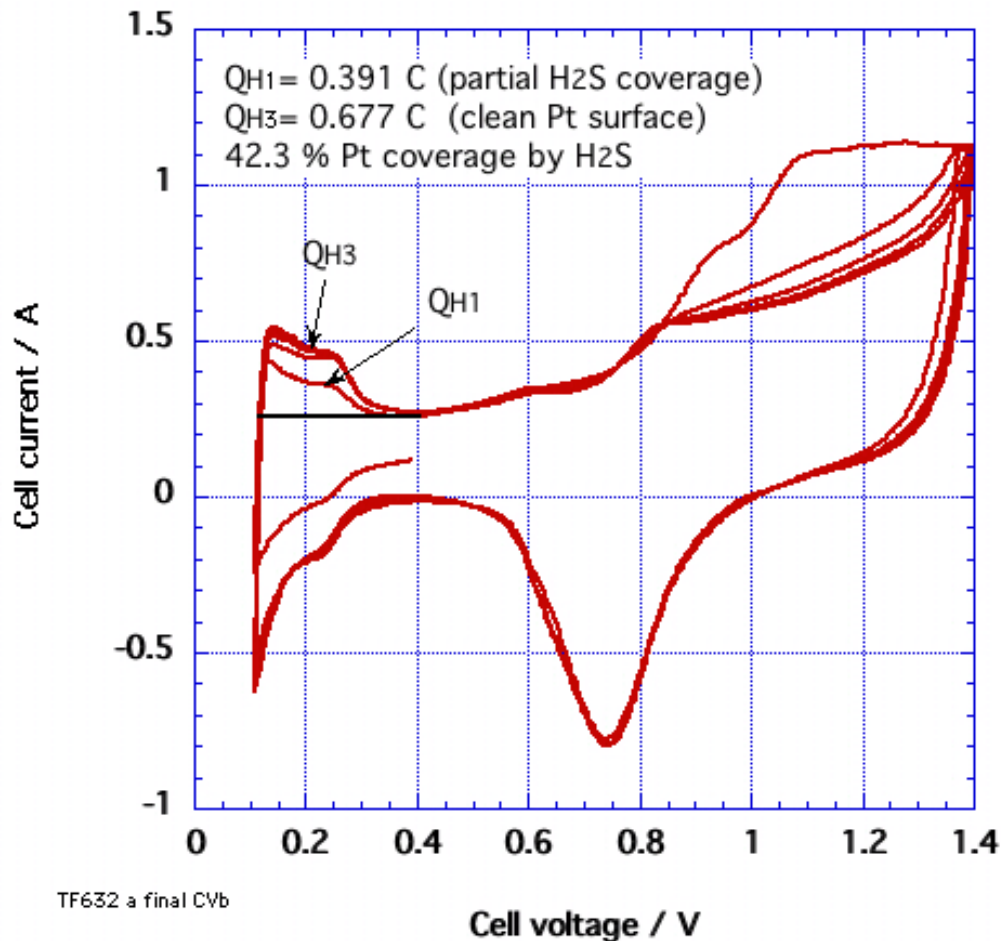


TF631 2 HFR

- High frequency resistance increases with time for impurity test mixture
- 25 mV loss from R increase
- NH₄⁺ exchange for H⁺ ?
- IR loss is not the only source of cell voltage drop

• Ammonia gas forms cations and lowers membrane conductivity

Impurity Mixture Effects



TF632 a final CVb

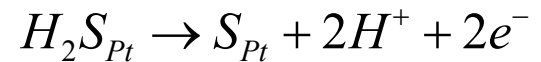
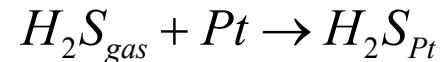
50 cm² cells / N112, 50 mV/s
 Loadings: 0.2 mg Pt at each electrode
 Cell Temperature: 80 °C. PSIG: 30/30

- Cyclic voltammetry is indicative of sulfur poisoning: ~40% coverage of Pt surface

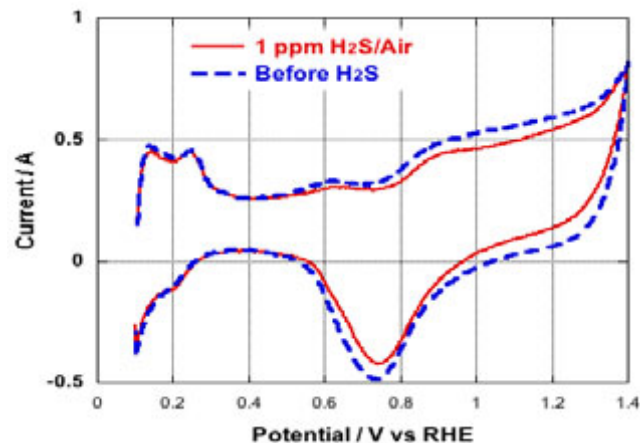
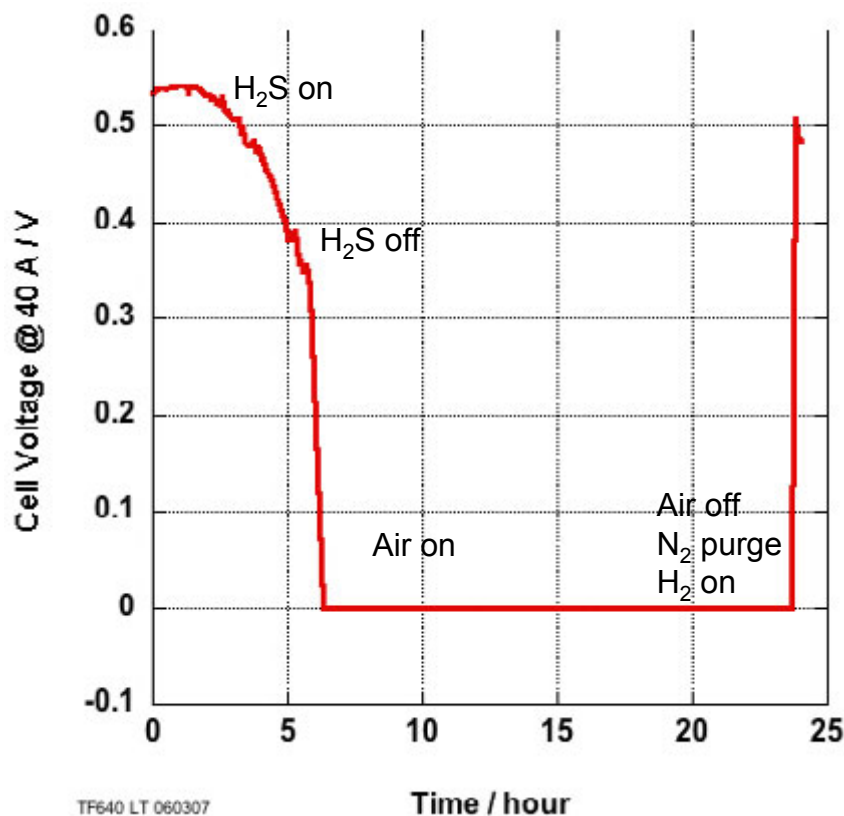
- No Evidence of CO in CV

- S adsorbed onto Pt strongly blocks CO adsorption in gas phase studies:
V.D. Thomas et al. Surface Science 464 (2000)

¹⁵³⁻¹⁶⁴
 Possible reactions:

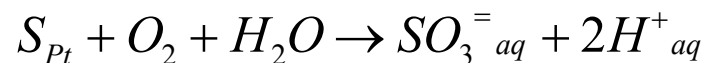
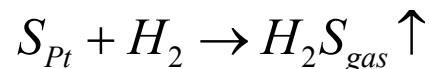


Milestone: Air Effect on Anode Due To Shut-down



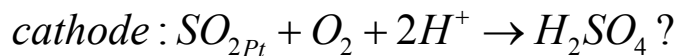
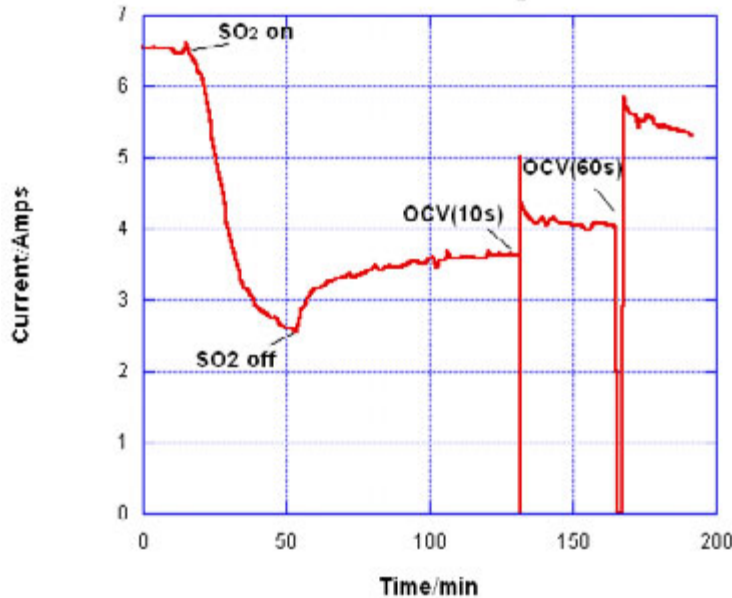
- Anode poisoned with 1 ppm H₂S
- Anode is at OCV before air exposure
- Air bled overnight
- Cell recovered almost fully

Possible mechanisms?

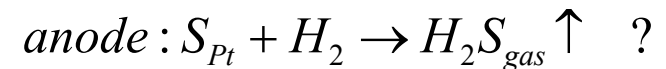
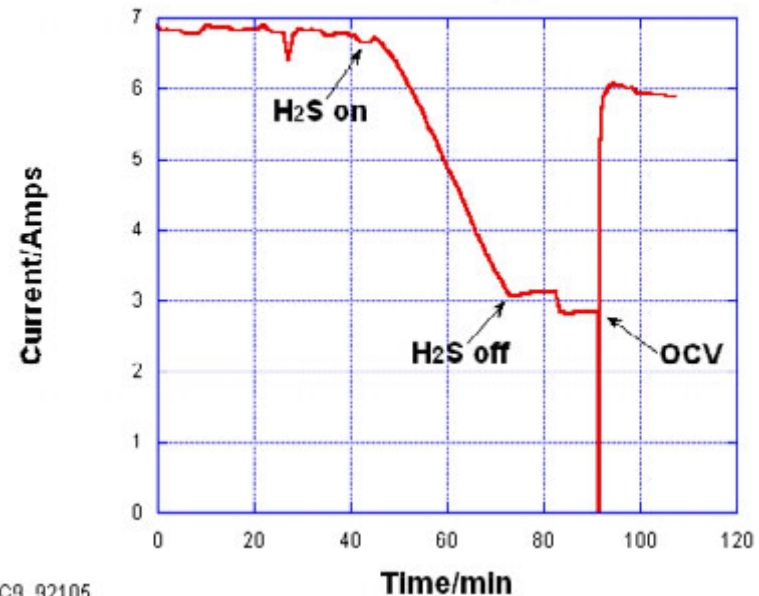


Effect of OCV on Sulfur Poisoned Cathodes and Anodes

Effects of OCV on Cell Performance exposed to 10 ppm SO₂



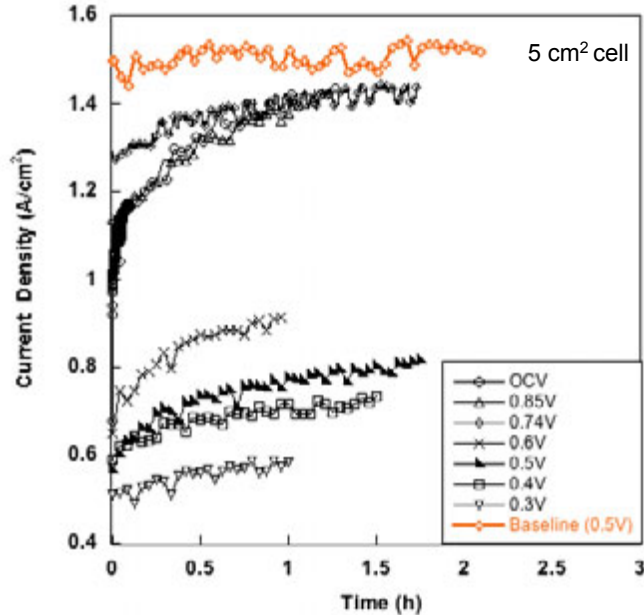
Effect of OCV on Cell Recovery of a Pt-Anode Poisoned with 2 ppm H₂S



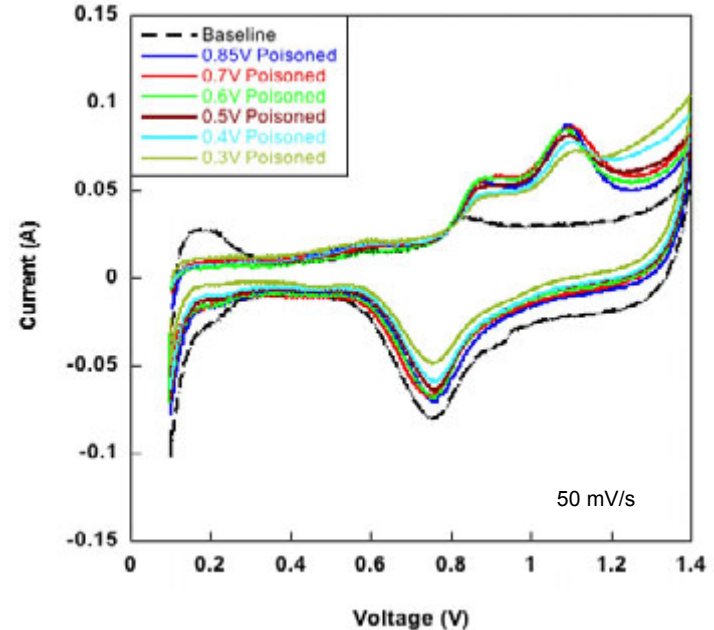
- Cells are poisoned for 50 min (2X amount of H₂S needed for full poisoning at 100% adsorption efficiency)
- The application of Open Circuit Voltage on S-poisoned electrodes indicates partial recovery

Effect Of Cell Voltage on H₂S Anode Poisoning

Cell performance recovery (at 0.5 V) after anode exposure to H₂S at different voltages



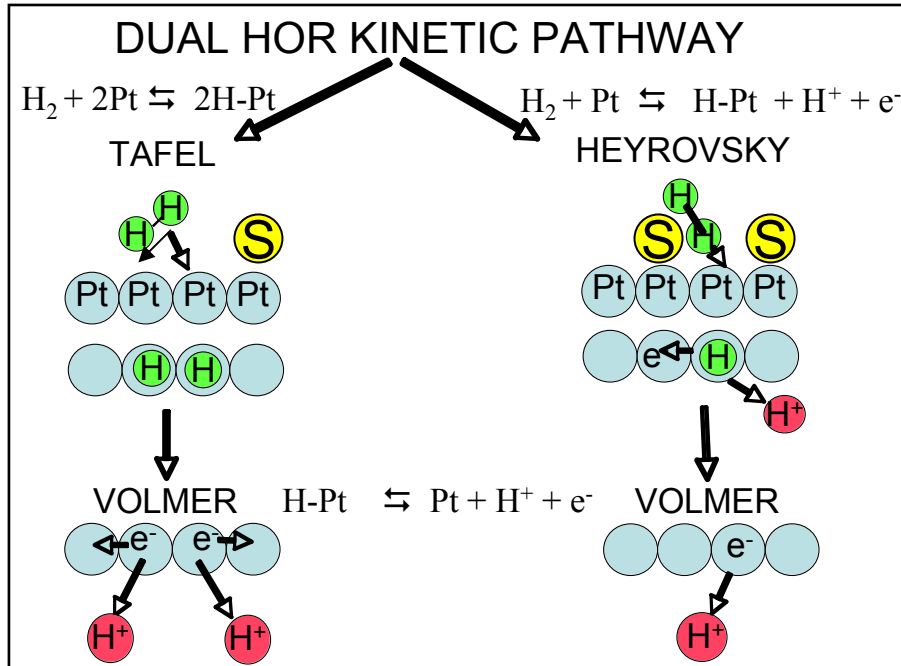
CV's for H₂S poisoned anodes at different cell voltages



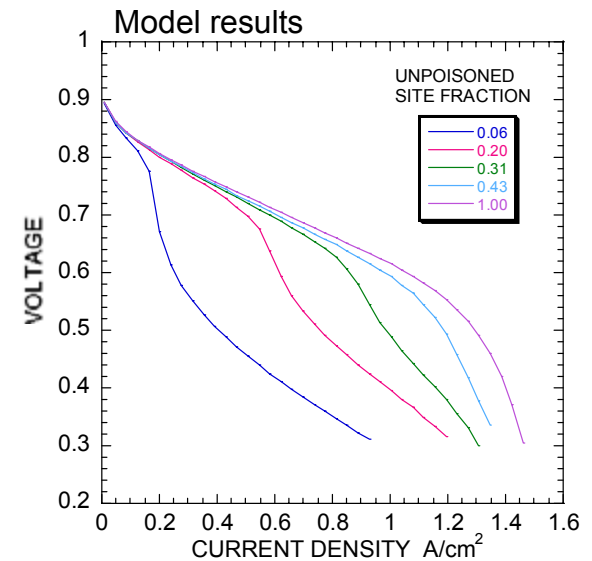
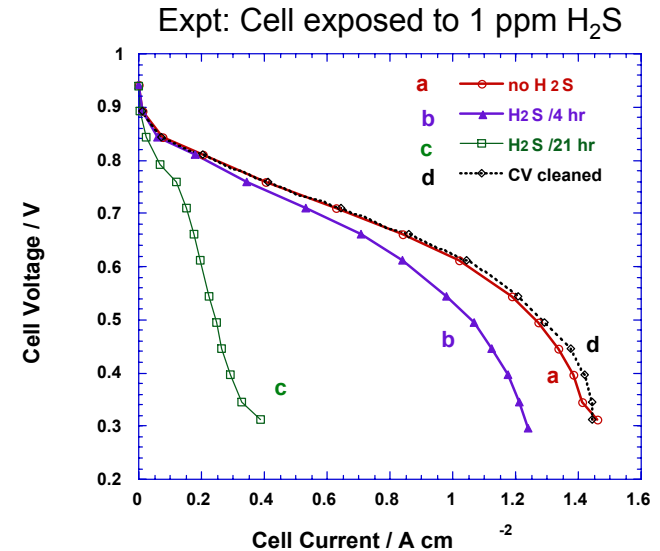
- Cell voltage at which H₂S exposure occurs influences amount of performance loss and recovery rate
- More poisoning at low cell voltages

Operating Voltage / V	Q _{anodic} / C	Q _{oxide reduction} / C	Q _{Sulfur} / C
0.85	0.0315	0.0123	0.0192
0.74	0.0342	0.0108	0.0234
0.6	0.0349	0.0109	0.0241
0.5	0.0341	0.00977	0.0243
0.4	0.0350	0.0107	0.0242
0.3	0.0338	0.00952	0.0243

Hydrogen Oxidation Model Aids Understanding of Impurity Effects

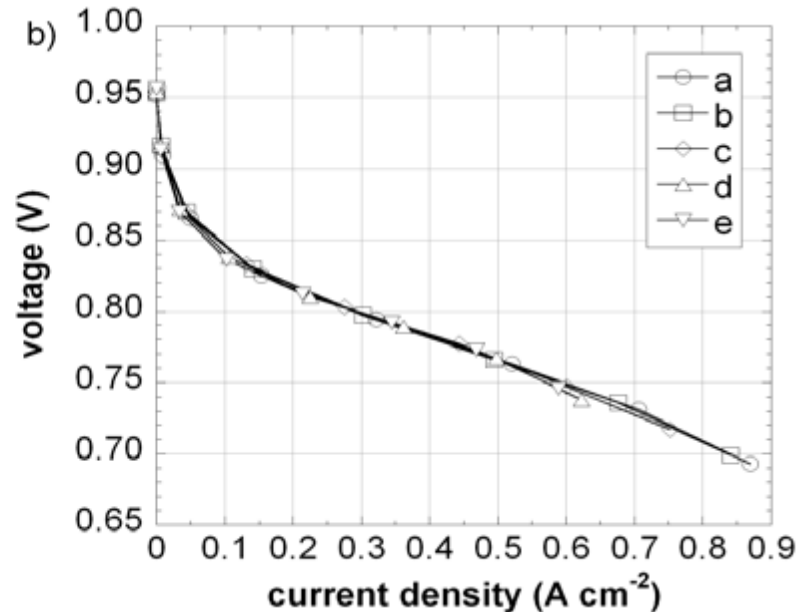
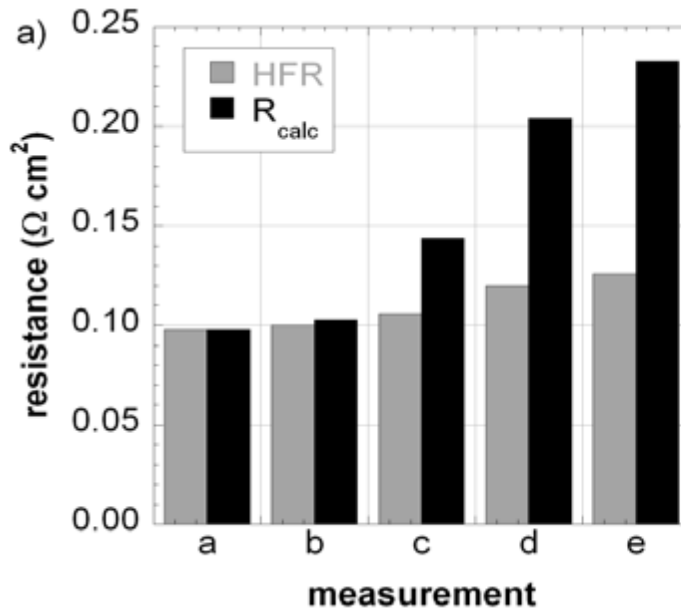
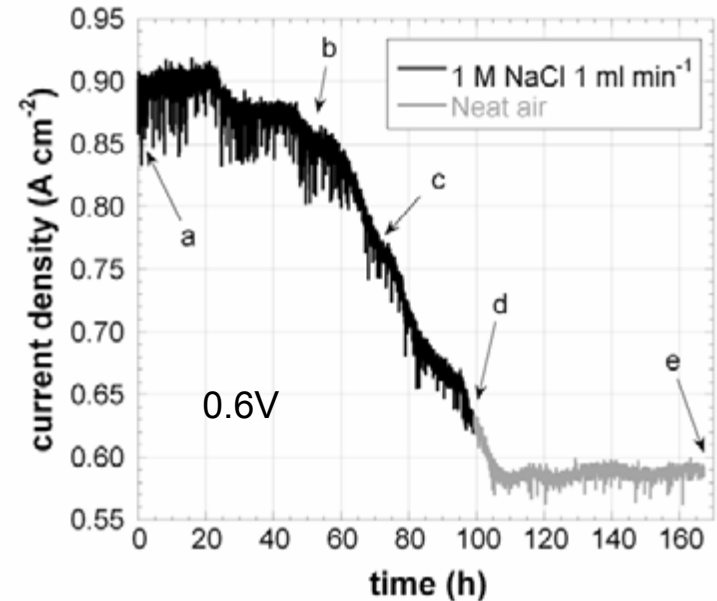


- Dual path HOR kinetics model needed to explain H₂S poisoning data
- S poison acts as an irreversible H site blocker
- Old Butler-Volmer kinetics cannot explain results



Modeling NaCl Contamination

- NaCl was introduced with the air feed (at high concentration and flow rate – enough Na^+ for complete exchange every 15 seconds)
- CVs show Cl^- at cathode plays no role
- HFR measures ion conductivity (combination H^+ and Na^+)
 - IR corrections necessary for VI agreement much larger
 - HFR (complete Na^+ exchange) $\sim 171 \text{ m}\Omega/\text{cm}^2$



Summary

- H₂S in fuel test mixture is primarily responsible for anode polarization losses
 - Little effect from CO in mixture-competitive adsorption
 - Almost no adsorption onto XC-72 but other carbons behave differently
- Ammonia is ion exchanging for protons and causing conductivity losses
- SO₂-poisoned cathode can be partially cleaned at OCV
- Fuel cell operating voltage strongly affects extent of anode H₂S poisoning
- On shut-down OCV appears to be also an important factor for cleaning H₂S poisoned anode
- Air purging H₂S contaminated anode results in partial performance recovery
- Dual H oxidation pathway model provides insights in fuel cell behavior

Future Near Term Work

- Continue H₂S studies and begin SO₂ adsorption on other materials components of the fuel cell
 - Pt immersed in aqueous solution
 - Pt/XC-72R
 - Carbon paper
- Continue investigation of impurity speciation on Pt surfaces
- Determine performance threshold of H₂S and NH₃ allowed in fuel
- Elucidate cleaning mechanism by OCV in S-poisoned electrodes
- Continue development of impurity models
- Characterize effects of H₂S on anode durability and SO₂ on cathode durability
- Measure effects of Ca and Mg salt ions on fuel cell performance
- Commence particulate injection studies

Publications, Presentations and Patents

- M. Mikkola, T. Rockward, F. Uribe and B. Pivovar, *"The Effect of NaCl in Cathode Air Stream on PEMFC Performance,"* Submitted to *Fuel Cells - From Fundamentals to Applications* (2006).
- F. Uribe and T. Rockward, *"Cleaning (de-poisoning) PEMFC electrodes from strongly adsorbed species on the catalyst surface"* 104229 Non-Provisional patent application (2006).
- F. Uribe and T. Rockward, *"Cleaning PEMFC Electrodes with Adsorbed S-species"*. 208 ECS Meeting, Los Angeles, CA. October (2005)
- F. Uribe *et al*, *"Electrode Structures and η Effects Of Fuel Cell Impurities"* invited talk INRS, Quebec Canada, (2006)

Review Comments

- Focus on basic understanding rather than empirical testing
 - We are coupling electro-analytical studies to reaction pathway modeling for first principles understanding.
- Focus on component generated impurities rather than fuel impurities
 - LANL & ORNL have previously and are currently studying fuel cell impurity generation and membrane uptake from metallic bipolar plates. The FreedomCAR tech team has suggested this project research priorities focus on fuel impurities.
- Increase interaction with FreedomCAR Codes and Standards Team
 - We have a project member participating at all FCCS meetings and we have tested their proposed impurity limits mixture.